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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Process for the Preparation of Metal Hydroxide

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Notice: This application is as filed and may therefore contain an
incomplete specification.



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A process for the preparation of metal hydroxides

Abstract

Process for the preparation of metal hydroxides and/or metal oxides/hydroxides from corresponding metal ions and hydroxide ions, whereby the metal ions are formed in an electrochemical membrane process in which the metal ions are formed by anodic dissolution of corresponding metals in the anode compartment and the hydroxide ions by cathodic reduction of water in the cathode compartment separated by an anion-exchange membrane, and the hydroxide ions are transferred through the anion-exchange membrane into the anode compartment under the driving force of an electric field.

A process for the preparation of metal hydroxideBACKGROUND OF THE INVENTION

5 The present invention relates to a process for the preparation of metal hydroxides and/or metal oxides/hydroxides from corresponding metal ions and hydroxide ions, in which the metal ions are formed in an electrochemical membrane process by anodic dissolution of corresponding metals in the anode compartment and the hydroxide ions by cathodic reduction of water in the cathode compartment
10 through the anion-exchange membrane into the anode compartment under the driving force of an electric field.

Metal hydroxides and metal oxides/hydroxides are valuable intermediates for the preparation of inorganic or organic salts of said metals, for the corresponding oxides, or the pure metals themselves. For example, a cobalt oxide of defined
15 composition e.g. for use in electronics for the production of varistors or in batteries, may be prepared from cobalt hydroxide by calcining or, by reduction, a cobalt metal powder of defined particle size distribution. Nickel hydroxides are used as pigments or are used with various dopants and particle structures for use in batteries. Zinc hydroxides may be used as starting materials for pigments and
20 the copper compounds can be converted into catalytically active materials.

During the preparation of hydroxides for various applications, the primary aim is to prepare, if possible, compact and free-flowing material for further processing. Cobalt metal powder, prepared from cobalt hydroxide or cobalt oxide/hydroxide, yields a particle size distribution and particle structure such that it can be sintered
25 together with tungsten carbide to produce products such as, e.g. special carbide-tipped structures.

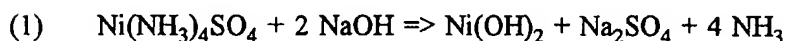
For the newly developed foam anodes which are used particularly in nickel hydride storage cells, a nickel hydroxide is required the physical properties of which are optimized both in terms of the application and the processing technique used. Use in high-performance batteries with nickel foam electrodes (based on
5 paste technology) requires a material with good flow properties, a compact particle form, narrow particle size distribution and consistent quality. Moreover, the product should have the ability to mix readily with the conventionally used additives such as, e.g., cobalt metal powder and cobalt oxide.

10 A corresponding material and main features of the production process are described in Japanese patent Hei 4-80513. Nickel hydroxide particles with a diameter between 1 and 100 μm are crystallized through a nickel salt solution and an alkali hydroxide, in solid or liquid form, being introduced continuously into a reaction vessel at a constant pH and a constant temperature. A pH of 11 and a temperature of 48 $^{\circ}\text{C}$ are given as favorable test conditions.

15 It is also known that the preparation of a sufficiently compact nickel hydroxide may be carried out by precipitation in the presence of ammonia or an ammonium salt. According to Trans. Faraday Soc. 51 (1955) 961, a nickel amine complex solution is prepared from nickel nitrate and aqueous ammonia solution, from which a nickel hydroxide is obtained by boiling at customary or reduced pressure
20 or by treatment with steam. Such a hydroxide has a much lower specific surface area (13 to 20 m^2/g) compared with the nickel hydroxides that are precipitated in the absence of ammonia. The preparation of compact nickel hydroxides in the presence of ammonia or an ammonium salt is also disclosed by the Japanese patent applications A 53 6119 and A 61-18107. In the first patent application
25 mentioned, the precipitation of nickel hydroxide by the addition of an alkaline solution to a corresponding solution with a pH of at least 3.0 is described. Electrochemical tests on the material prepared in this way revealed particularly high specific charge capacities compared with commercial nickel hydroxides.

Such products do not yet, however, fulfill the above-mentioned requirements in terms of particle form, particle size distribution and flow properties.

Important features of the process for the preparation of a compact nickel hydroxide and the use thereof in alkaline batteries are described in European patent application A 353 837. A nickel (II)-tetrammine salt solution is prepared by dissolution of nickel nitrate or nickel sulfate in dilute ammonia solution and decomposed by controlled addition of sodium hydroxide solution in accordance with the following reaction:



The reaction takes place at temperatures between 40 and 50 °C and in the pH range between 11 and 13. The pore volume falls as the pH falls. It has been ascertained that a pore-free product may be crystallized only at sufficiently low rates of reaction. Moreover, the nickel hydroxide prepared according to said process has a high crystallinity, a low specific surface area, a low pore volume and therefore a high physical density. The disadvantages of said product, which are attributable to the high density, are also described. The low specific surface area results in a lower proton conductivity and in a higher current density which promotes the production of unwanted γ -NiOOH, which leads to swelling of the electrode. Although the nickel hydroxide crystallised at low pH values has a high density, it has a greater tendency to form γ -NiOOH. Due to the choice of a mean pH, a compromise may be found between the required high density and the porosity required to a certain extent. According to said process, a nickel hydroxide is prepared which contains 3 to 10% of zinc and 1 to 3% of magnesium in solid solution. Said dopants counteract the production of γ -NiOOH.

A continuous process for the crystallization of a nickel hydroxide with spherical particle form is implied from the patent JP Hei 4-68249. In said process, a nickel salt solution (0.5 to 3.5 mole/l), dilute alkaline solution (1.25 to 10 mole/l) and an ammonia and/or ammonium salt solution are pumped continuously by means of

metering pumps, with intensive stirring, into a heated cylindrical container provided with an overflow pipe, it also being possible for the ammonia to be introduced in gaseous form. The ammonia concentration is given as 10 to 28% by wt. and the ammonium salt concentration as 3 to 7.5 mole/l. In order to complex the nickel, between 0.1 and 1.5 mole of ammonia per mole of nickel salt solution are introduced. After about 10 to 30 hours, the system reaches a stationary state, after which a product with consistent quality may be removed continuously. The residence time in the container is between 0.5 and 5 hours.

An important feature of said process is the fact that the reaction is carried out at a defined pH which is kept constant to ± 0.1 pH levels in the region between 9 and 12 by the pH-controlled introduction of alkaline solution, and at a constant temperature in the region between 20 and 80 °C, whereby the temperature deviations should not be more than ± 2 K. Under these conditions, the compact spherical particles are obtained with a particle size of between 2 and 50 μm . The particle size can be adjusted in particular by varying the NH_3 inflow, the residence time and the stirring speed. As the stirring speed decreases and the NH_3 inflow increases, the particle size increases. As the residence time in the container increases, the product becomes coarser, the particle size distribution narrower. The crystalline product is then filtered, washed with water and dried. The product prepared according to said process has the properties mentioned at the beginning, and does not need to be ground.

A process for the preparation of nickel hydroxide is disclosed in European patent application A 462 889. The temperature range of crystallisation is above 80 °C. Nitrate or sulphate solutions doped with cobalt, cadmium and/or zinc are used. The cobalt content is between 1 and 8% by wt., and the contents of cadmium and/or zinc are between 3 and 10% by wt. Complexing takes place with the aid of an ammonium salt, the molar ratio of NH_3/Ni being between 0.3 and 0.6. In said process, a pH of 9.2 ± 0.1 is maintained. Moreover, a three-blade stirrer, the diameter of which is half as great as the diameter of the container and the rate of rotation of which is between 300 and 1000 min^{-1} is used.

As in the processes already described, the product is filtered, washed and dried.

5 The disadvantages of said processes are, on the one hand, the large quantities of neutral salts inevitably produced, which are at least twice the stoichiometric quantity of nickel hydroxide and are released into the effluent. On the other hand, the effluents of these processes contain, in addition to small quantities of nickel dissolved in the form of complexes, large quantities of ammonia which must be disposed of.

10 In the chemical process of precipitation crystallization for the preparation of spherical nickel hydroxide, 2 mole of sodium chloride per mole of nickel hydroxide are inevitably produced. In view of more stringent environmental guidelines and limits for effluent, on the one hand, and economic considerations due to the high consumption of liquor and resulting landfill costs for the salt produced, on the other hand, closed production circuits must be developed.

15 In such a process, nickel, for example, is dissolved anodically in a metal salt solution by electrolysis, and precipitated as nickel hydroxide by the cathodically formed hydroxide ions. After sedimentation and various successive washing stages to purify the precipitated product of any salts still present or entrapped during precipitation, the pure product is obtained.

20 Processes for the preparation of metal hydroxides are already described in the following patents.

25 In Japanese patent application A 63/247 385, the electrolytic preparation of metal hydroxides is carried out using a perfluorinated anion-exchange membrane of Toyo Soda and the use of inert electrodes. The metal salt of the metal hydroxide to be prepared is used as the electrolyte on the anode side. In the cathode circuit, an alkaline solution is used.

In European patent application A 0 559 590, in a comparable arrangement, the metal salt is added continuously by anodic dissolution of the electrode. The requirements regarding the process, particularly the membranes to be used, the electrolyte solutions and the test conditions are specified only insufficiently.

- 5 The object of this invention is to provide a process for the preparation of metal hydroxides and/or metal oxides/hydroxides which does not have the disadvantages of the prior art described.

SUMMARY OF THE INVENTION

- 10 This object is achieved by a process for the preparation of metal hydroxides and/or metal oxides/hydroxides from corresponding metal ions and hydroxide ions, whereby the metal ions are formed in an electrochemical membrane process by anodic dissolution of corresponding metals in the anode compartment and the hydroxide ions by cathodic reduction of water in the cathode compartment bounded by an anion-exchange membrane, and the hydroxide ions are transferred
15 through the anion-exchange membrane into the anode compartment by the driving force of an electric field, whereby the dissolution of the metals is carried out in the presence of complexing agent at a pH of >7 .

- Preferably ammonia and/or organic mono- and/or diamines with a chain length of 1 to 6 C atoms are used as complexing agents within the meaning of this
20 invention. Metals are, in particular, one or more from the group Co, Ni, Cu, Fe, In, Mn, Sn, Zn, Zr, Ti, Al, Cd and Ni. Co and/or Ni are particularly preferred. The process according to the invention will be described hereinafter for the case of the preparation of nickel hydroxide without thereby restricting the invention.

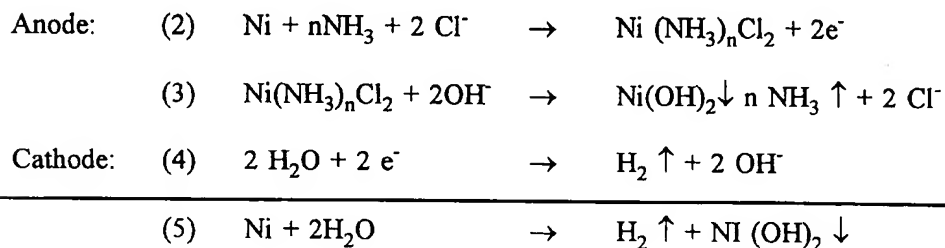
- 25 The configuration arising in principle for a membrane electrolytic cell which is suitable for carrying out the process according to the invention is presented below. The cathode compartment and anode compartment of the electrolytic cell are separated by an anion-exchange membrane such that two separate circuits are

produced. The circuit on the side of the cathode is called the catholyte and that on the anode side the anolyte. Alkaline solutions such as preferably sodium hydroxide solution or potassium hydroxide solution are used as catholyte. It is advantageous for the efficiency of the process if the solution itself has a high conductivity and the cation of the alkaline solution used is also used on the anode side. The cathode itself may be composed of quenched and tempered steel, platinized titanium, nickel, or a nickel alloy.

The composition of the anolyte is obtained from the starting products for the preparation of nickel hydroxide, i.e. ammonia, sodium chloride and small quantities of nickel sulfate. The sodium chloride is used primarily to increase the conductivity of the solution, and the anodic dissolution of the nickel electrode is improved by the small addition of sulphate. Particularly good results are obtained when chloride and/or sulfate ions are present in the anolyte. The anode itself is composed of pure nickel, preferably an electrochemically produced anode.

In the preparation of other metal hydroxides and/or metal oxide/hydroxides, the anode is composed of the corresponding metals. In principle, therefore, a sacrificial anode is used.

Under active transport conditions in view of the external potential applied, nickel dissolves as Ni^{2+} ion, releasing electrons. The presence of ammonia prevents the spontaneous precipitation of $\text{Ni}(\text{OH})_2$ under alkaline conditions and leads via various intermediate stages to a divalent nickel-amine complex.



The reaction at the cathode yields hydrogen, with electron uptake, which escapes in gaseous form, and hydroxide ions which are transported in accordance with their charge via the anion-exchange membrane into the anode circuit. The formation and precipitation of the nickel hydroxide then takes place in the anolyte
5 when the solubility limit is exceeded. Precipitation follows a dynamic equilibrium, ligand exchange (ammonia for hydroxide) taking place.

The formation of the spherical product is determined essentially by the crystallization conditions, i.e. the concentration of the individual components and the temperature control in the anode circuit. The precipitated product is then
10 separated continuously from the anolyte circuit. Separation may be carried out in a sedimentation tank that is simple to design from a process technology angle in view of the great difference in density between the product formed and the solvent. Separation takes place via a filtration stage (microfiltration) in order to separate a product of uniform particle size. The essential advantage of said
15 process variant is that additional individual process stages for recovering the various starting products are not required since they are kept in the anolyte circuit.

In order to put into practice the electrochemical membrane process described, it is necessary to ensure that the anion-exchange membrane to be used fulfils the following requirements:

- 20 It must be resistant to alkalis, in particular, chemically stable in the adjacent solutions (to NH_3 up to the saturation concentration), resistant to oxidation ($\text{Ni}^{2+}/\text{Ni}^{3+}$; Cl^- , ClO_3^-), temperature-resistant up to 80°C , it must have a high permselectivity, a low membrane resistance, high mechanical strength and dimensional stability and sufficient long-term stability.
- 25 Industrially relevant ion exchange membranes usually have a microheterogeneous and/or interpolymer morphology. The aim to be achieved thereby is that the mechanical and electrochemical properties may be membranes adjusted in isolation. Accordingly, a membrane is constructed from a matrix polymer, a

fabric or a binder, and from a polyelectrolyte or an ionomer. A distinction is made among homogeneous membranes, interpolymer membranes, microheterogeneous graft or block copolymer membranes and heterogeneous membranes according to the degree of heterogeneity of the ion exchange membrane.

- 5 The polymer network may have a different structure in order to exhibit sufficiently good electrical and mechanical properties for most applications. Polyvinyl chloride and polyacrylate is normally used as the electrically neutral matrix polymer. Polyethylene, polypropylene or polysulphone may be used as other matrix polymers, only these having long-term chemical stability under alkaline
10 conditions.

In the process according to the invention, therefore, an anion-exchange membrane is preferably based on polyethylene, polypropylene, polyether ketone, polysulphone, polyphenyloxide and/or sulfide.

- 15 The ion-conducting polyelectrolytes of an anion-exchange membrane are composed of a network with a positive excess charge and mobile, negatively charged counterions. The fixed ion structure may be built up by weakly basic amino and imino groups, and from strongly basic ammonium and quaternary ammonium groups:



- 20 It is particularly preferred that the anion-exchange membrane used in the process of the invention have exchange groups of alkylated polyvinyl imidazole, polyvinyl pyridine and/or alkylated 1,4-diazabicyclo[2.2.2]octane.

Particularly suitable membranes are described in German patent application A 42 11 266.

The type and concentration of fixed ions determines mainly the permselectivity and the electrical resistance of the membrane, but it may also influence the mechanical properties, particularly the swelling of the membrane in view of the concentration of fixed ions. The strongly basic quaternary ammonium group is dissociated at all pH values, while the primary ammonium group is dissociated only with difficulty. For this reason, mostly quaternary ammonium groups are incorporated in commercial anion-exchange membranes except if a membrane with particular properties is to be produced.

Systems based on chloromethylated polystyrene, styrene/divinylbenzene copolymers and styrene/butadiene copolymers with subsequent quaternization with trimethylamine are used most frequently.

The long-term chemical stability of the anion-exchange membranes may be influenced only by the following factors:

- destruction of the polymer matrix (inadequate stability of the matrix polymer or interpolymer in alkaline solution)
- morphological change of the fixed ion structure/polymer matrix system
- chemical degradation of the fixed ion under alkaline or oxidative conditions.

The electrochemical, mechanical and chemical properties must be optimized in the same way for the selection of an anion-exchange membrane for use in the preparation of spherical nickel hydroxide by membrane electrolysis from ammoniacal solution. This means that requirements in terms of membrane and material selection and the physico-chemical properties produced by the manufacturer must be drawn up and evaluated. Said requirements may be summarized as follows for the membranes used according to the invention:

As regards the electrochemical properties, the

- electrical resistance should be $<10 \Omega \cdot \text{cm}^2$
- the permselectivity $>92\%$
- the swelling $<25\%$, and
- 5 the ion exchange capacity $>1.2 \text{ mmole.g}^{-1}$.

As regards the mechanical properties, the fabric should be composed of

- temperature-, alkali- and oxidation-resistant polymers
- (polypropylene, polyethylene, polyether ketone)
- and have, as a fixed loading
- 10 chemically stable quaternary ammonium salt
- (vinyl imidazole, 4,4'-diazabicyclo[2.2.2]octane).

- Suitable membranes are described in German patent application 44 21 1266. It is particularly preferred that the process according to the invention be carried out continuously, the metal hydroxide and/or metal oxide/hydroxide formed being
- 15 separated from the anolyte and the complexing agent being returned to the anode compartment.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The invention is explained by way of example below, without any restriction being implied therein.

Example 1 Preparation of cobalt hydroxides

Structure of the electrolytic cell in principle

The electrolytic cell is shown in attached Fig. 1. It is composed of two nickel cathodes, two polyethylene spacers, two membranes and the cobalt sacrificial anode and four compartments of varying thickness. The cell is constructed in such a way that the nickel cathodes represent the outer sides of the cell with a surface area of $120 \times 200 \text{ mm}^2$ of effective electrode surface. The electrical contacting takes place on superimposed electrode surfaces. On the cathode lies a polyethylene frame 5 mm thick on which in turn the membrane lies. The gap between the membrane and the cobalt anode is maintained by a further frame 10 mm thick, which anode lies above the frame and is provided with the electrical leads. The cobalt anode is composed of pure cobalt with a thickness of 20 mm. The entire structure is pressed together in a liquid-tight manner by means of a support. A polyethylene lattice core mesh is inserted between the cathode and the membrane, which lattice prevents contact between cathode and membrane. The frames that separate anode and membrane are provided with holes through which the anolyte enters and leaves. The cathodes are similarly provided with inlets at the cathode-membrane separating frames such that a uniform flow with the catholyte is guaranteed in the entire cathode compartment.

20 The catholyte and anolyte each contain 100 g/l of NaCl. The catholyte also contains 40 g/l NaOH.

The catholyte is pumped round (recirculated) at a speed of 100 l/h, which corresponds to a residence time of the electrolyte of 9 seconds in the cathode compartment. The anolyte is pumped in a recirculating circuit during electrolysis at a rate of 650 l/h which corresponds to an average residence time of 2.7 seconds in the anode compartment. The temperature of the anolyte is 50 °C. The ammonia concentration in the anolyte is adjusted to 2 mole/l and losses by evaporation are offset by the addition of ammonia to the anolyte circuit.

The stationary solids concentration of cobalt hydroxides formed is 80 g/l with an average residence time of 4 h.

5 The electrolysis conditions are chosen such that a current of 12 A corresponding to 500 A/m² flows, whereby 21 g of cobalt hydroxide in the form of Co(OH)₂ are formed each hour, which are expelled from the circuit in a 0.26 l suspension and separated by filtration. After washing with water, a clean cobalt hydroxide is obtained. The hydrogen formed is expelled from the catholyte storage container.

pH anolyte: 10.5-11.5

Membrane: Neosepta® AMH, manufactured by Tokuyama Soda

10 Composition of the end product:

Cobalt hydroxide, mixture of Co(OH)₂ with CoOOH in a ratio of 80/20 according to analysis.

Bulk density: 1.6 g/cm³

Cobalt content: 63.5%

15 Color: Dark brown.

Example 2 Preparation of nickel hydroxide

In an electrolytic cell which is constructed in a comparable way (as in Example 1) as a stack of electrodes and membranes with the electrode compartments in between, nickel is dissolved electrochemically in the presence of ammonia, and
20 the amine complex formed decomposes to nickel hydroxide.

Electrolyte composition:

Anolyte: 16.5 mole/l NiSO₄

220 ml NH₃ (25%)/l

- 2 mole/l NaCl
- Catholyte: 1 mole/l NaOH
- Anode: Ultra-pure nickel
- Cathode: Platinized titanium
- 5 Temperature: Electrolysis 40 °C
Decomposition of the complex 70 °C
- Current density: 1000 A/m²
- Gap between electrode/membrane: 2 mm
- Overflow speed: >10 cm/s
- 10 pH anolyte: 10.5-11.5
- Membrane: Neosepta® AMH manufactured by Tokuyama Soda

The decomposition of the amine complex formed in electrolysis to nickel hydroxide is carried out by raising the temperature of the electrolyte in a reactor.

a) Preparation of a compact, spherical nickel hydroxide

- 15 The amine complex is decomposed in a stirred reactor whereby the decomposition product agglomerates to compact, spherical particles. The agglomerated material is separated continuously as a suspension from the circuit of the anolyte via an overflow.

Nickel hydroxide from the overflow:

- 20 Bulk density: 1.35 g/cm³
Mean particle size: 10 μm

b) In the presence of substrates such as fibers of nickel or a spherical ion exchange resin with the mean particle size of 200 μm, a uniform layer of nickel hydroxide is deposited on the substrate in the decomposition reactor.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the preparation of metal hydroxides and/or metal oxides/hydroxides from corresponding metal ions and hydroxide ions, wherein the metal ions are formed in an electrochemical membrane process by anodic dissolution of corresponding metals in the anode compartment and the hydroxide ions by cathodic reduction of water in the cathode compartment bounded by an ion-exchange membrane, and the hydroxide ions are transferred through the ion-exchange membrane into the anode compartment under the driving force of an electric field, characterized in that the dissolution of the metals is carried out in the presence of a complexing agent at a pH greater than 7.
2. Process according to claim 1, wherein the complexing agent is selected from the group consisting of ammonia C_{1-6} - organic monoamines and C_{1-6} - organic diamines.
3. Process according to claim 1, wherein the metal is selected from the group consisting of Co, Ni, Cu, Fe, In, Mn, Sn, Zn, Zr, Ti, Al, Cd and U.
4. Process according to claim 1, wherein the metal is selected from the group consisting of Co and Ni.

5. Process according to claim 1, wherein the catholyte is an aqueous alkaline solution.
6. Process according to claim 1, wherein the anolyte includes chloride or sulphate ions.
7. Process according to claim 4, wherein the anolyte includes chloride sulphate ions.
8. A process according to any one of claims 4, 5 or 6 wherein the complexing agent is selected from the group consisting of ammonia, C₁₋₆- organic monoamines and C₁₋₆- organic diamines, the metal is selected from the group consisting of Co, Ni, Cu, Fe, In, Mn, Sn, Zn, Zr, Ti, Al, Cd and U.
9. A process according to any one of claims 4, 5 or 6 wherein the ion-exchange membrane is a membrane based on a compound selected from the group consisting of polyethylene, polypropylene, polyether ketone, polysulphone, polyphenyloxide and sulphide.
10. A process according to claim 9, wherein the ion-exchange membrane has exchange groups selected from the group consisting of alkylated polyvinyl imidazole, polyvinyl, pyridine and alkylated 1,4-diazabicyclo [2.2.2]octane.

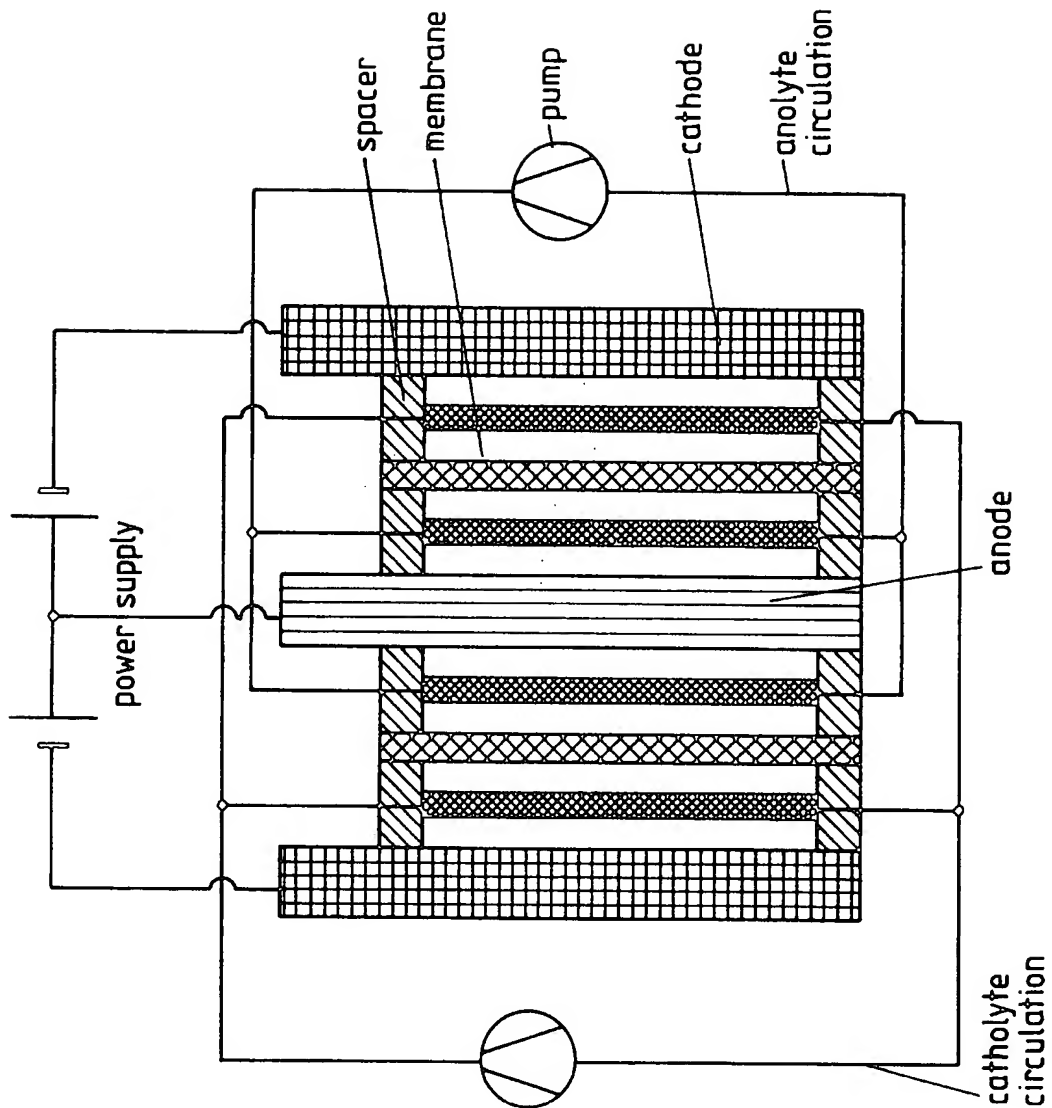
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11. A process according to any one of claims 4, 5, or 6 wherein the metal hydroxide and/or metal oxide/hydroxide formed is separated from the anolyte and the complexing agent is returned to the anode compartment.

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